

Experimental study of the three-dimensional ac conductivity and dielectric constant of a conductor-insulator composite near the percolation threshold

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We measured the ac conductivity and dielectric constant of a three-dimensional randomly mixed conductor-insulator system consisting of amorphous carbon and Teflon powder in the frequency range from 10 Hz to 13 MHz. Near the percolation threshold, these two quantities varied as a power of ω , such as $\sigma \sim \omega^x$, and $\epsilon \sim \omega^{-y}$. The values of x and y were found to be 0.86 ± 0.06 and 0.12 ± 0.04 , respectively. These values are compared to the present percolation theories. We also measured the dc conductivity exponent t and dielectric constant exponent s to complete the study. Our data yielded $t = 1.85 \pm 0.25$ and $s = 0.68 \pm 0.05$.

I. INTRODUCTION

The critical behavior of the effective conductivity σ and dielectric constant ϵ of normal metal-insulator composite systems has been the subject of extensive studies in both theory and experiment.¹⁻¹³ According to percolation theory, near the percolation threshold concentration p_c , there exists a characteristic correlation length ξ proportional to $|p - p_c|^{-\nu}$. This correlation length, which diverges from either side of the metal-insulator transition, is related to many intrinsic properties of the composite: for example, the probability of belonging to the percolating cluster $P(p)$ is proportional to $\xi^{-\beta/\nu}$ or $|p - p_c|^\beta$ for $p > p_c$. The scaling hypothesis asserts that properties of physical quantities such as the dc electrical conductivity $\sigma(\omega=0, p > p_c)$ and the dc dielectric constant $\epsilon(\omega=0, p < p_c)$ of a percolating system should exhibit a power-law dependence on the correlation length ξ . On the conducting side of the transition ($p > p_c$), $\sigma(0, p)$ is proportional to $\xi^{-t/\nu}$ or $|p - p_c|^t$. On the insulating side ($p < p_c$), $\epsilon(0, p)$ is proportional to $\xi^{s/\nu}$ or $|p - p_c|^{-s}$. These power laws are supposed to be universal; that is, the critical exponents depend primarily on the dimensionality of the percolating systems and not on the details of the geometric structures or the interactions.

Recently, there has been interest in the ac conductivity $\sigma(\omega, p)$ and the dielectric constant $\epsilon(\omega, p)$. By using some general analytic properties of the effective complex dielectric constant of a random mixture expressed as a function of the dielectric constant of each constituent, Bergman and Imry¹⁴ derived the following power-law behavior for $\sigma(\omega, p_c)$ and $\epsilon(\omega, p_c)$:

$$\sigma(\omega, p_c) \sim \omega^x, \quad (1)$$

$$\epsilon(\omega, p_c) \sim \omega^{-y}, \quad (2)$$

near the percolation threshold. These critical exponents, x and y , are supposed to satisfy the following equation:

$$x + y = 1, \quad (3)$$

if $\sigma(\omega, p)$ and $\epsilon(\omega, p)$ both obey scaling forms that have a

single characteristic time scale.

The frequency dependence of the effective conductivity and the dielectric constant of the random mixture results from two important effects: (a) polarization effects between clusters inside the mixture and (b) anomalous diffusion within each cluster. Considering only the inter-cluster polarization effects, many workers^{6,14-17} have derived

$$x = t/(t+s), \quad y = s/(t+s). \quad (4)$$

Recently, Gefen *et al.*¹⁸ studied the anomalous diffusion on the percolating clusters. By using the Einstein relation,¹⁹ they obtained

$$x = t/\nu(2+\theta), \quad y = (2\nu-\beta)/\nu(2+\theta), \quad (5)$$

for $\omega \gg \omega_\xi \sim \xi^{-(2+\theta)}$, where ω_ξ^{-1} is the diffusion time for a distance ξ and θ is a new critical exponent which describes the diffusion process for short times. [θ is given by $\theta = (t-\beta)/\nu$.] Note that the Eqs. (4) and (5) satisfy the general scaling relation of Eq. (3).

The above two approaches will lead to the same results if $s = 2\nu - \beta$, which holds for the effective medium theory,²⁰ where $s = 2\nu - \beta = 1$, and for the mean-field calculation⁸ which gives $s = 2\nu - \beta = 0$. However, according to the recent percolation theories, the equality $s = 2\nu - \beta$ does not hold when the dimension $d=3$ ($s \sim 0.7$, $2\nu - \beta \sim 1.3$) or when $d=2$ ($s \sim 1.3$, $2\nu - \beta \sim 2.5$).²¹ A unified theory which includes both effects is presently not available.

Recently, along with these theoretical approaches, Laibowitz and Gefen²² investigated the ac conductivity and dielectric constant for thin gold films near their percolation threshold. The thickness of these two dimensional samples was chosen in such a way so that the insulator-metal transition was spanned. The variation of the thickness between samples was only several angstroms. The frequency range covered by them was from 100 Hz to 10 MHz. The power-law behavior as predicted in Eqs. (1) and (2) was observed. For their two-dimensional (2D) samples, they found $x = 0.95 \pm 0.05$ and

$y=0.13\pm 0.05$. These values are in good agreement with the general scaling relation, i.e., Eq. (3), but they are significantly different from present theoretical predictions [in $d=2$, $x=y=0.5$ from Eq. (4) or $x\sim 0.33$ and $y\sim 0.67$ from Eq. (5)].

In this paper, we present results of our experiments on the ac conductivity and dielectric constant near the percolation threshold for a three-dimensional randomly mixed conductor-insulator system consisting of amorphous carbon and Teflon powder. In order to show that the critical phenomena of our samples followed the percolation theories and to complete the systematic study, we measured the dc conductivity and dielectric constant. We found that they obey very well the scaling power laws, with the conductivity exponent t equal to 1.85 ± 0.25 and the dielectric constant exponent s equal to 0.68 ± 0.05 . The measurement of the ac conductivity and dielectric constant was performed on samples near the percolation threshold for frequencies between 10 Hz and 13 MHz. In the critical region, the power-law behavior of Eqs. (1) and (2) was observed with $x=0.86\pm 0.06$ and $y=0.12\pm 0.04$, in agreement with the general scaling relation $x+y=1$. These values are closer to the prediction of the intercluster polarization model, Eq. (4) (in $d=3$, $x\sim 0.72$, and $y\sim 0.28$) than that of the anomalous diffusion model, Eq. (5) (in $d=3$, $x\sim 0.58$, and $y\sim 0.42$). It is interesting to note that these values are close to the experimental results of Laibowitz and Gefen²² on two-dimensional gold films.

The samples used in this experiment were three-dimensional randomly mixed conductor-insulator composites. These kinds of samples have been studied for a long time in order to understand the physical behavior of inhomogeneous media, such as the transport and optical properties.²³ Along with the recent development of the percolation theories, these systems have been used to find the critical exponents s and t .¹¹ Recently, these systems were also used to study the behavior of $1/f$ noise near the percolation threshold.²⁴ The technique we used for making and characterizing them are given in Sec. II, and the data are presented and discussed in Sec. III.

II. EXPERIMENTAL PROCEDURES

We used Teflon powder as the insulating component since this powder is very stable, easy to mix, and free from the water contamination compared to other typically used insulators such as KCl or KBr.¹⁰ Initially, we used silver powder for the conducting component, but the low resistivity of the silver powder made the silver-teflon composites unsuitable for accurate conductivity studies. Since our measurements were done between 1 Ω and 100 M Ω the low resistivity of the silver limited the possible range of the conductivity measurement to the region very close to p_c . This small measurement range made it very hard to get reliable results. Therefore, we used amorphous carbon powder as the conducting component. The low conductivity of the carbon powder made it possible to easily observe the changes of conductivity as a function of p . This powder has been used by several other workers²⁴⁻²⁶ to study percolation behavior.

Our samples were prepared by mixing the carbon and

Teflon powder preweighed to the desired volume fractions. The composite of these two components was roughly mixed in a vial by a vortex mixer, then it was cooled down to liquid-nitrogen temperature and repeatedly ground by using a Spex freezer mill. The mixture was then taken out of the vial, heated up to room temperature, and compressed in an evacuated die to a pressure of about 100 000 psi, forming a solid pellet. For the purpose of improving the randomness, the sample was put into the freezer mill again and the previous process was repeated. After two cycles of grinding and compaction, a certain amount of the well-mixed powder was pressed into a pellet $\frac{5}{8}$ in. in diameter and about 1 mm in thickness. The final compaction was performed under a vacuum in the 10^{-6} -Torr range. This repeated grinding and compaction process in our sample preparation is a standard procedure¹⁰ used to produce a uniform distribution of conducting particles inside an insulator. To insure that we had a uniform distribution, we took scanning electron microscope (SEM) pictures of our samples.

In order to have good electrical contact for the conductivity and dielectric constant measurement, we coated the pellets on both faces with a 1000-Å-thick silver layer, using a bell-jar system at 10^{-6} Torr. The room-temperature dc resistance of our samples was measured by the four-probe method. The dielectric constant was measured using a lock-in amplifier and a three-terminal 1615A General Radio capacitance bridge. The bridge was operated at 100 Hz with a peak to peak voltage amplitude of 400 mV.

The ac conductance and capacitance, which are proportional to the ac conductivity and dielectric constant respectively, were measured simultaneously using a Hewlett Packard 4192A Impedance Analyzer with a four-probe geometry. The data acquisition process was controlled by a PDP-11 computer through the IEEE-488 bus cable. This automated process made it possible to perform measurements repeatedly so that the signal to noise ratio was improved by a factor of about 5 over the single sample measurement. Typically, about 10 measurements were repeated for each frequency point with 20 frequency points distributed in a logarithmic scale for each decade. The frequency range we scanned was 10 Hz to 13 MHz. Since the voltages applied were small (peak-to-peak voltage of 0.4 V), no destructive effect was observed.

III. RESULTS AND DISCUSSION

The result of the dc resistance measurements is plotted in Fig. 1. By using a least-squares fit (the solid line in Fig. 1), we found the conductivity exponent t and the percolation threshold p_c . The conductivity exponent was found to be $t=1.85\pm 0.25$, in good agreement with the well-established value.²¹ The value obtained for the percolation threshold $p_c=0.290\pm 0.005$ agrees with our experimental observation that the samples with conducting material concentration less than p_c have a resistance in excess of 100 M Ω .

In Fig. 2, the measured capacitance, which is proportional to the dielectric constant, of the samples is plotted on a logarithmic scale. The solid line is the best fit to the scaling relation $\epsilon \propto (p_c - p)^{-s}$. As stated in Sec. II, we

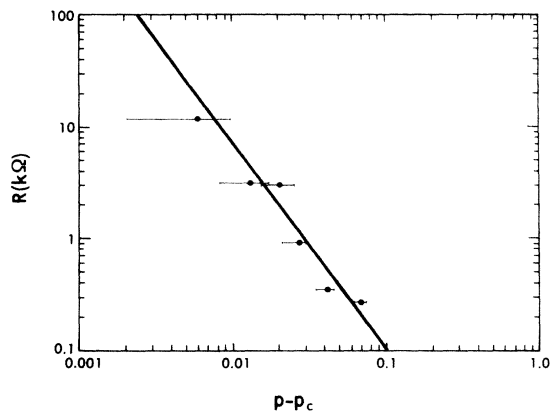


FIG. 1. Plot of dc resistance as a function of $p - p_c$. The solid line is the best fit to $R \sim (p - p_c)^{-t}$. $p_c = 0.290 \pm 0.005$ and the conductivity exponent $t = 1.85 \pm 0.25$. The flags attached to the data points represent the error in determining the volume fraction only. Other errors would increase the size of the flags.

used a frequency of 100 Hz to measure the capacitance of our samples. However, according to Efros and Shklovskii,¹⁵ $\epsilon(\omega, p < p_c)$ will follow the same power-law behavior as $\epsilon(0, p < p_c)$, i.e., $\epsilon(\omega, p < p_c) \propto (p_c - p)^{-s}$, if the measuring frequency ω is sufficiently low. Therefore, the dielectric constant exponent s obtained from Fig. 2 should be same as the dc dielectric constant exponent. The least-squares fit gives $s = 0.68 \pm 0.05$ in agreement with the earlier experiment done by Grannan *et al.*¹⁰ Moreover, the estimated value of $p_c = 0.290 \pm 0.005$ is consistent with our result from the conductivity measurement.

The percolation threshold p_c of our samples is larger than the generally accepted values of $p_c = 0.15 - 0.20$ for a continuous percolation system,^{4,10,27} or $p_c = 0.07 - 0.11$ from former experiments on a carbon-wax system.^{24,25} This larger value of p_c can be understood from the SEM pictures we took. As we can see in Fig. 3, the teflon has a tendency to surround the carbon powder, so the carbon clusters are separated by a thin insulator layer. This kind of behavior has been observed in many granular compos-

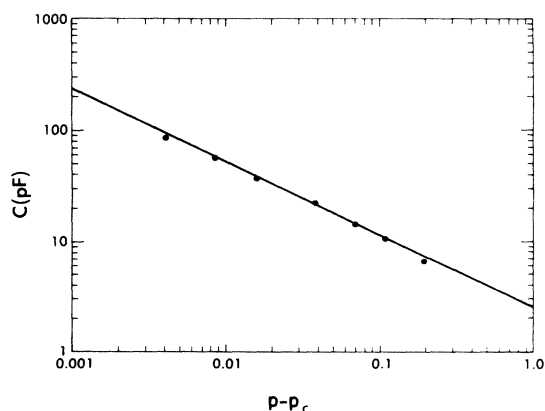


FIG. 2. Data of dc capacitance versus $p_c - p$. The solid line is the best fit to $C \sim (p_c - p)^{-s}$. The dielectric constant exponent s was found to be 0.68 ± 0.05 .

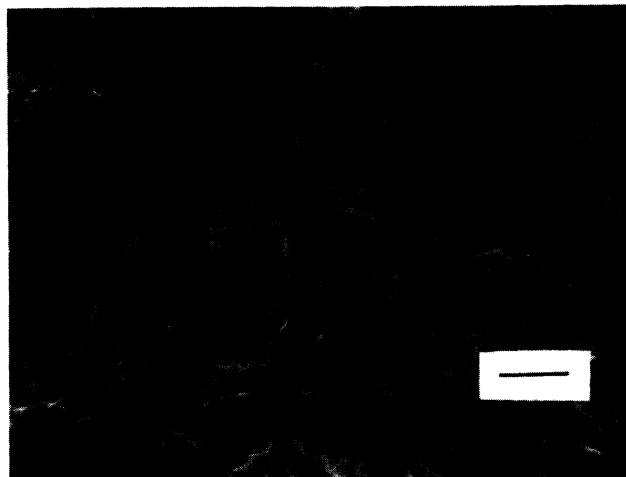


FIG. 3. Scanning electron microscope picture of one of the carbon-Teflon mixture samples. The bright patterns are Teflon clusters. The carbon clusters in the dark area are surrounded by the Teflon clusters. The volume fraction of the carbon powder is 28%. The line mark represents $20 \mu\text{m}$. Since this sample is pretty close to the percolation threshold, the size of the carbon clusters is relatively large.

ites¹¹ or discontinuous films,^{28,29} which always show a higher value of p_c than the predicted value. According to the universality hypothesis, the critical exponents do not depend on the details of cluster structures or interactions. Supporting this hypothesis, most of the critical exponents observed in the granular composites of discontinuous films usually agreed with that of the random composites.¹¹ Therefore, even though our samples showed a high value of p_c , our dc conductivity and dielectric constant measurements still followed the predictions of the percolation theories.

Figure 4 is a log-log plot of the ac conductance of

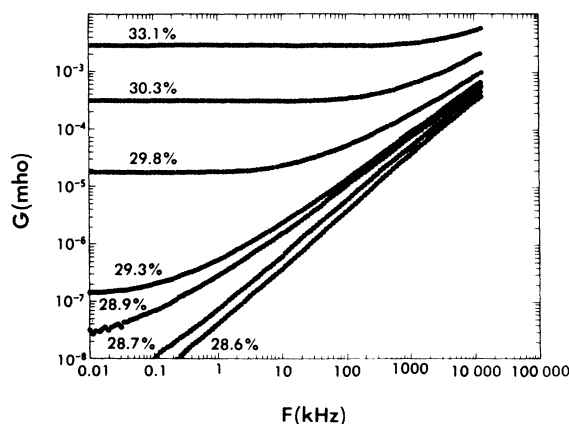


FIG. 4. Logarithmic plot showing the ac conductance of carbon-Teflon mixture samples versus frequency. Data were displayed for samples having different concentrations, with numbers on each data line representing the volume fraction of the carbon powder. The 28.9% sample is just below the percolation threshold. The critical exponent x was found from this graph to be 0.86 ± 0.06 .

several carbon-Teflon mixture samples as a function of the applied frequency. The carbon-powder volume fractions p of the samples in the graph ranged from 28% to 34%, bracketing the critical region. For our samples with volume fraction $p < p_c$, there exists some frequency above which the ac conductivity is measurable with our apparatus. This ac conductivity linearly increases with signal frequency on a log-log plot, demonstrating the power-law behavior. The samples which are above p_c , on the other hand, have a flat response to low frequency input signals. A transition region exists where the response starts to bend upward at high frequencies, and eventually becomes a linearly increasing straight line, again showing power-law behavior. Notice that for samples with a higher p value the transition region where the ac conductance starts to bend is located at even higher frequencies. It is also obvious that there is no distinction between the insulating phase and the conducting phase at high frequencies in the critical region: the ac conductance of samples which are just above p_c and those just below p_c all yield straight lines with same slope. From these curves, we obtained the critical exponent $x=0.86\pm 0.06$.

The frequency dependence of $\sigma(\omega, p > p_c)$ can be explained in part in terms of the polarization effects^{6,14-17} by making an analogy between our sample and an equivalent circuit which has capacitance between the different clusters. If p is significantly larger than p_c , then the conductivity is mainly determined by the many paths of the percolating clusters rather than the small effect of the capacitors. Therefore, the conductance of the sample will not change significantly up to a certain frequency, above which the contribution of the capacitors becomes important. On the other hand, near the critical region, there exist only a few percolating paths of clusters, so the contribution of the capacitors between clusters becomes very important. As the frequency increases, the current passing through each capacitor increases resulting in the increased conductivity of the sample.

In addition to the intercluster polarization effects, the anomalous diffusion inside the clusters¹⁸ also contributes the frequency dependence of $\sigma(\omega, p > p_c)$. The conductivity of most conductors has a flat response in the frequency range of our experiments, since electrons can move freely over arbitrarily large distances in an applied field. For highly conducting samples, electrons can still move through the many paths of the infinite clusters, so this flat response is maintained. However, at $p \sim p_c$, only a few paths of percolating clusters are available, so the motion of the electrons in the finite clusters becomes very important. At a certain frequency ω , electrons will scan a distance L_ω . If $L_\omega < \xi$, the conducting clusters are self-similar fractals, so $L_\omega \sim \omega^{-1/(2+\theta)}$. Since the conductivity increases when L_ω decreases,³⁰ from the above equation, we can see that the conductivity will increase with increasing ω .

Below the percolation threshold, due to a lack of percolating clusters, the polarization between the clusters and the motion of electrons in the finite cluster will determine $\sigma(\omega, p < p_c)$. Therefore, $\sigma(\omega, p < p_c)$ increases as the frequency increases. It is expected that a sample below p_c will follow $\sigma(\omega, p < p_c) \sim \omega^2$ at low frequencies,¹⁵ since the

dissipation of energy due to the polarization of isolated conducting clusters will dominate in the insulating phase. A smooth transition from ω^x behavior to ω^2 behavior is expected to take place for samples near p_c . However, as shown in Fig. 4, even for samples near p_c the asymptotic ω^2 behavior is not observed for frequencies above 100 Hz.

Figure 5 is a logarithmic plot of the capacitance versus frequency for our carbon-Teflon samples. In the low-frequency region, the capacitance of samples far from p_c has a flat response to the input signals, similar to the ac conductance behavior. In the high frequency region (> 1 MHz), the responses of different samples become parallel, indicating that they follow the same power law. The critical exponent y was found from this graph to be $y=0.12\pm 0.04$.

We now compare our numerical values of the critical exponents x and y with the theoretical predictions presently available. The theoretical prediction based on intercluster polarization gives $x=t/(t+s)$ and $y=s/(t+s)$. Using the recently available values of $t \sim 1.8$ and $s \sim 0.7$ for $d=3$, we get $x \sim 0.72$ and $y \sim 0.28$. However, the recent calculation¹⁸ based on anomalous diffusion gives $x=t/\nu(2+\theta)$ and $y=(2\nu-\beta)/\nu(2+\theta)$, for which the estimated values are $x \sim 0.58$ and $y \sim 0.42$. Our measured values, $x=0.86\pm 0.06$ and $y=0.12\pm 0.04$, are closer then to the prediction of the intercluster polarization model than they are to the prediction of the anomalous diffusion model for the measured frequency range of our samples. It is possible that the anomalous diffusion effect might be more important for even higher frequencies. Our measured values of x and y do satisfy the general scaling relation, $x+y=1$.

Our experimental values of $x=0.86\pm 0.06$ and $y=0.12\pm 0.04$ were close to the measured values, $x=0.95\pm 0.05$ and $y=0.13\pm 0.05$, from two-dimensional

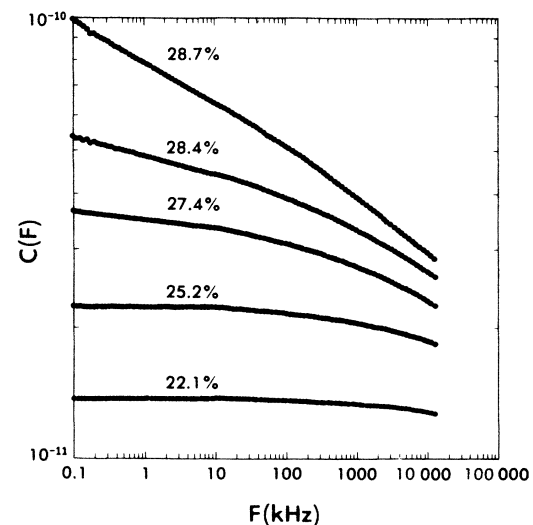


FIG. 5. Data of ac capacitance versus frequency. The samples are all on the insulating side. The exponent y was found to be 0.12 ± 0.04 .

discontinuous gold films.²² This was quite interesting, since the universality hypothesis states that the critical exponents depend on the dimensionality. Our three-dimensional randomly mixed carbon-Teflon system approximately followed the prediction of the intercluster models, while the results on the two-dimensional gold films have not been explained satisfactorily by a percolation approach.

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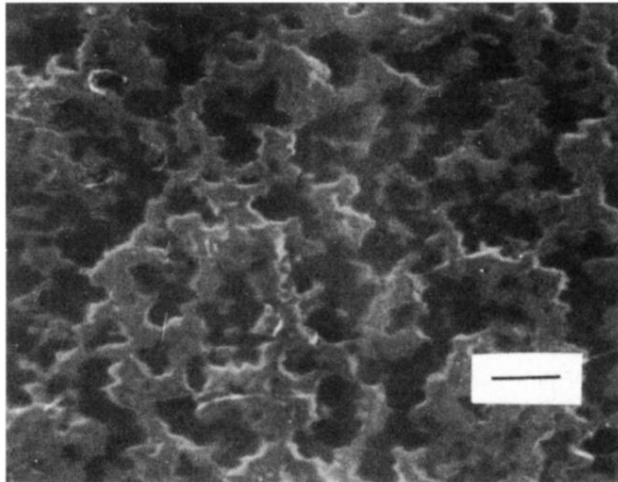


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